

# PATENT SPECIFICATION

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 (72) Inventors RODERICK BASIL JUDGE and  
 DONALD BEREND DENNEY

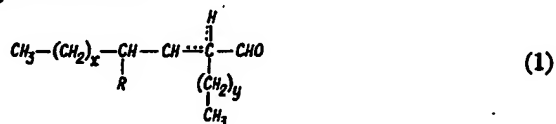


## (54) UNSATURATED ALDEHYDES, THEIR PRODUCTION AND CONVERSION

(71) We, W. R. GRACE & CO., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 1114, Avenue of the Americas, New York, New York 11036, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of aldehydes having a chain of at least 5 carbon atoms, in good yield, by an aldol reaction of two simpler aldehydes. Certain aldehydes produced by the process of this invention are novel compounds, which per se are part of the invention. They can be used in making esters which are useful as base stocks for lubricants.

The aldehydes of this invention (and which may be prepared by the process of this invention) have the general formula

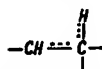


wherein

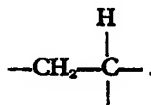
x is 1, 2, 3 or 4,

y is 0, 1, 2 or 3,

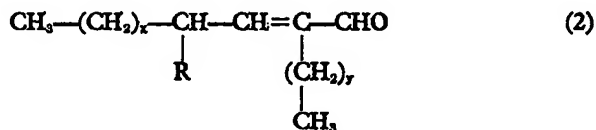
R is an alkyl group having 1 to 4 carbon atoms and the symbol



represents either the unsaturated group  $-\text{CH}=\text{C}-$  or the saturated group

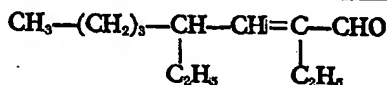


The unsaturated aldehydes within the above general formula (1) have the following general formula:



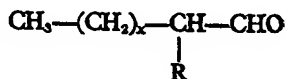
wherein x, y and R have the same meanings as in formula (1).

So far as we know, even the simplest aldehyde of general formula (2) is, by itself, novel and the others are all novel. The preferred unsaturated aldehyde of this invention is that wherein x is 3, y is 1 and R is ethyl, namely

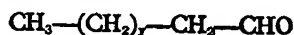


which is 2,4-diethyl-oct-2-en-1-al.

Unsaturated aldehydes of formula (2), but in which x can be 0, 1, 2, 3 or 4 and y can be 0, 1, 2, 3 or 4 can be made by the well-known aldol condensation, reacting two aldehydes in the presence of alkali metal hydroxide, wherein the first aldehyde has the formula



and the second aldehyde has the formula



x, y and R being as required for the unsaturated aldehyde product.

According to the process of the present invention, the aldol condensation using these reactants is effected in a reaction medium comprising an aqueous alkali metal hydroxide solution and a phase transfer catalyst, hereinafter abbreviated to PTC. As is apparent from results given below, use of PTC leads to a much greater yield and much greater conversion of starting material than when the aldol condensation is effected in the absence of PTC.

Phase transfer catalysts are well known; they are taught by:

1. Starks *et al*, South African Patent No. 71/01,495 (Chemical Abstracts, 76, 1972, 153191g).

2. Starks, J. Am. Chem. Soc., 93, 1971, 195.

3. Starks *et al*, J. Am. Chem. Soc., 95, 1973, 3613.

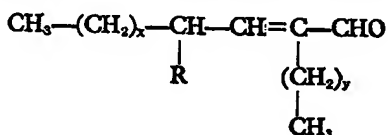
However the use of such catalysts in aldol reactions is believed to be novel.

The aldol addition which is also called the aldol condensation or the aldol reaction is well known. See for example:

1. Pages 333—337 of Day and Joulie, "Organic Chemistry", D. Van Nostrand Company, Princeton, New Jersey, 1960.

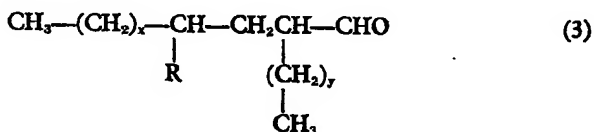
2. Pages 466—467 of Vol. 1, Part A, of Rodd "Chemistry of Carbon Compounds", Elsevier Publishing Company, Amsterdam, 1951.

3. Page 642 of Vol. 1 of the Second Edition of Kirk-Othmer, Encyclopedia of Chemical Technology, John Wiley and Sons, Inc., New York, 1963. It should be understood that the invention includes the above-defined aldol condensation process using a phase-transfer catalyst to produce aldehydes of formula



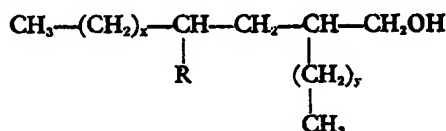
wherein R is as defined above, x is 0, 1, 2, 3 or 4 and y is 0, 1, 2, 3 or 4.

The unsaturated aldehydes mentioned above, i.e. aldehydes of formula (2) howsoever prepared and aldehydes of formula (2) but in which x=0, 1, 2, 3, or 4 and y=0, 1, 2, 3 or 4 prepared by the above-defined aldol condensation reaction of the invention, employing a phase transfer catalyst, can be hydrogenated to saturated aldehydes having the formula



where x, y and R are as defined in the starting, unsaturated aldehyde. The preferred saturated aldehyde of formula (3) is 2,4-diethyloctanal.

By hydrogenation of the saturated aldehydes of formula (3), or by continued hydrogenation of the unsaturated aldehydes, there can be produced alcohols of formula:



of which 2,4-diethyloctanol is the preferred example. x, y and R are as defined in the starting saturated or unsaturated aldehydes.

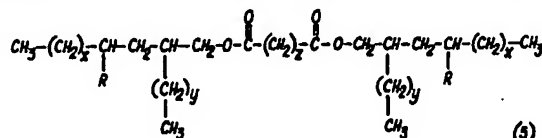
In the above process, preferred values for x are integers from 1 to 3 (especially 3). Preferred values for y are integers from 1 to 3 (especially 1), R is preferably  $-\text{CH}_2\text{CH}_3$ .

In an especially preferred embodiment of the above-described process x is 3; y is 1; R is  $-\text{CH}_2\text{CH}_3$ .

The above alcohols can be reacted with a dicarboxylic acid having the formula



where z is an integer from 1 to 12, to form an ester having the formula (5)



in which:

(a) x is 0 or an integer from 1 to 4;

(b) y is 0 or an integer from 1 to 4;

(c) R is an alkyl group having 1—4 carbon atoms; and

(d) z is an integer from 1—12 (preferably from 1—9),

the values of x, y and R being, of course, as in the alcohol of formula (4).

The preparation of esters in which both x and y are integers is not part of the present invention.

The esters of formula (5) are useful as base stocks for lubricants. These esters are especially useful as the major component of lubricants for jet engines, reciprocating (piston) engines, and the like, where high or low temperatures are encountered.

Esters of formula (5) in which x and y are integers from 1 to 4 are new compounds described and claimed as such in our Patent Application No. 14181/77 (Serial No. 1,547,857) which is a divisional of the present application. Their preparation from the corresponding alcohols, thence from the corresponding saturated and unsaturated aldehydes and thence from simpler aldehydes by the aldol reaction is also described and claimed in the divisional application.

When preparing the aldehyde of formula (2), preferably:

1. The mole ratio of the first aldehyde to the second aldehyde is from 20:1 to 1:1, most preferably 10:1 to 2:1.

2. The temperature of the reaction mixture is adjusted to and maintained at 50—150°C (most preferably 80—100°C).

3. The concentration of the alkali metal hydroxide solution is 4—50% (more preferably 5—15%), by weight. (All parts and percentages in this specification are by weight unless otherwise stated). Said alkali metal hydroxide solution will usually be KOH, LiOH, or NaOH solution. An amount of alkali metal hydroxide solution effective for promoting aldol addition is used. The amount of alkali metal hydroxide is not critical because a finite amount of said hydroxide solution produces a finite promotion of said aldol addition. We generally prefer to use 1 mole of said alkali metal hydroxide per 10—40 moles of first aldehyde (more preferably 1 mole of said hydroxide per 10—15 moles of said first aldehyde).

4. The exact amount of PTC is not critical because a finite amount of said catalyst produces a finite increase in the amount of product aldehyde formed. We generally use 1 mole of PTC per 50 to 200 moles of first aldehyde (more preferably about 1 mole of said catalyst per 100 moles of said aldehyde).

5. Contact time ("reaction time") under reaction conditions is not critical and generally varies from 1 to 2 or 1 to 3 hours. However, reaction rate is a function of reaction temperature and the longer contact times tend to be required at the lower temperatures recited above while the shorter times tend to be required at the higher temperatures. Thus, for the same conversion (one pass yield), a longer reaction time is required at 50°C than 80°C or 90°C or 125°C.

Typical PTCs which can be used with excellent results in the process of the invention include but are not limited to those listed in the Table below.

TABLE

The letters (a) to (d) refer to footnotes below.

5	Phase Transfer Catalysts (a)	5
	Lauryltrimethylammonium chloride	
	Dilauryldimethylammonium chloride	
	Trilaurylmethylammonium chloride	
	Myristyltrimethylammonium chloride	
10	Dimyristyldimethylammonium chloride	
	Trimyristylmethylammonium chloride	10
	Palmityl(cetyl)trimethylammonium chloride	
	Dipalmityldimethylammonium chloride	
	Tripalmitylmethylammonium chloride	
15	Stearyltrimethylammonium chloride	
	Distearyldimethylammonium chloride	15
	Tristearylmethylammonium chloride	
	Oleytrimethylammonium chloride	
	Dioleyldimethylammonium chloride	
20	Trioleylmethylammonium chloride	
	(Tall oil)trimethylammonium chloride (b)	20
	(Ditall oil)dimethylammonium chloride	
	(Tallow)trimethylammonium chloride (b)	
	(Ditallow)dimethylammonium chloride	
25	(Tritall oil)methylammonium chloride	
	Caprylyltrimethylammonium chloride (d)	25
	Dicaprylyldimethylammonium chloride	
	Tricaprylylmethylammonium chloride	
30	(Coco)trimethylammonium chloride (b)	
	(Dicoco)dimethylammonium chloride	30
	(Tricoco)methylammonium chloride	
	Decyltrimethylammonium chloride	
	Didecylmethylammonium chloride	
	Tridecylmethylammonium chloride	
35	Alkyldimethylbenzylammonium chloride (c)	
	Dialkylmethylbenzylammonium chloride (c)	35
	Laurylmethylethylpropylammonium chloride	
	Laurylethylmethylbutylammonium chloride	
40	Tetraurylammonium chloride	
	Dilaurylmethylethylammonium chloride	40
	Dipalmitylethylpropylammonium chloride	
	Tricaprylylmethylphosphonium chloride (b)	
	Dicaprylylmethylethylphosphonium chloride	
45	Caprylylmethylethylpropylphosphonium chloride	
	Stearyldipropylsulfonium chloride	45
	Distearylbutylsulfonium chloride	
	Tristearylsulfonium chloride	
	Oleyltributylarsonium chloride	
	Dioleyldiethylarsonium chloride	
50	Trioleylpropylarsonium chloride	
	Hexadecyltributylphosphonium bromide	50

## Footnotes to Table

(a) While the anion of most of the phase transfer catalysts listed in this table is shown, for convenience in preparing the table, as chloride, said anion can be substantially any anion such as bromide, iodine, fluoride, sulfate, phosphate or hydroxyl (OH-).

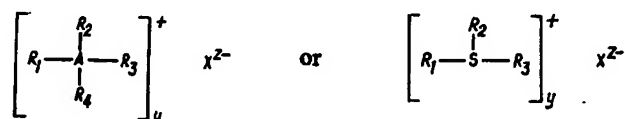
(b) As used herein the term "tall oil" means the mixed alkyl groups obtainable by reducing the fatty acids—predominantly oleic and linoleic acids—(or salts thereof) obtained by saponifying tall oil, "tallow" means the mixed alkyl groups obtainable by reducing fatty acids or salts thereof obtained by saponifying tallow, and "coco" means the mixed alkyl groups obtainable by reducing the fat (or "butter" or grease) obtained from coconuts. See pages 542—557 of Volume 1 of the Second Edition of the Kirk-

Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., New York, New York, 1963.

(c) As used in these compounds the term "alkyl" means an alkyl group (or a mixture of alkyl groups) each having 7—16 carbon atoms.

(d) "Caprylyl" is the C<sub>8</sub>-alkyl group from caprylic acid.

PTCs which can be used with excellent results in the process of this invention include but are not limited to those having the formula



in which:

(a) X<sup>z-</sup> is an anion (e.g. sulfate, phosphate, acetate, nitrate, chloride or bromide);

(b) z- is an integer denoting the number of negative charges on each anion;

(c) y is an integer equal to z, so that the cation and anion charges balance;

(d) R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are separately selected from (i) alkyl and alkenyl groups having 1 to 20 carbon atoms and (ii) aralkyl groups having 7 to 16, preferably 7 to 12 carbon atoms, e.g. benzyl;

(e) A is N, P or As. It is generally preferred that A be N or P.

Preferred PTCs include tricaprylylmethylammonium chloride and didecyl-dimethylammonium chloride.

Where preparing the product aldehyde of formula (2) of this invention we generally prefer to use the following general procedure which we have designated "Procedure A".

#### Procedure A

A predetermined amount of the first aldehyde is admixed with a predetermined amount of the second aldehyde to form a first admixture.

A predetermined amount of an aqueous solution of an alkali metal hydroxide (preferably NaOH, KOH, or LiOH) containing a predetermined amount of the alkali metal hydroxide is admixed with a predetermined amount of a phase transfer catalyst to form a second admixture. Excellent results can be obtained where using 5—15% NaOH, or KOH solution, or LiOH solution but more dilute and more concentrated alkali solutions can be used without decreasing one-pass-yield or quality of the product aldehyde.

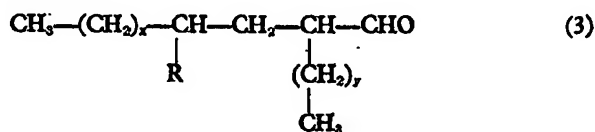
The second admixture is placed in a reaction zone provided with mixing (or agitating) means, heating means, an inlet port and an outlet port.

The first admixture is added to the second admixture over a predetermined period of time (e.g. 10—80 minutes, or 1—10 hours or 0.5—3 hours depending on the quantities and temperatures involved) while maintaining the temperature of the resulting reacting mixture within a range effective for forming the aldehyde of this invention. Such temperature can be any temperature (or temperature range) from 20 to 150°C and is preferably a temperature (or temperature range) from 60°C to 110°C. If desired, the mixture in the reaction zone can be maintained at such temperature (or within such temperature range) for a period of 15 minutes to 6 hours (or 0.5—1.5 hour) after all of the first admixture has been added to facilitate reaction.

The reacted mixture can be removed from the reaction zone and the product aldehyde recovered therefrom, e.g. by distillation of the reacted mixture using reduced pressure where necessary or desirable to facilitate recovery.

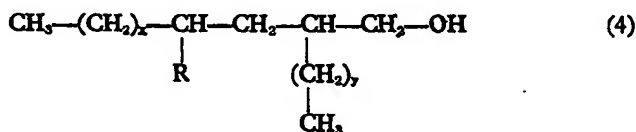
Unreacted starting aldehydes can be recovered and used in a subsequent run. Also side-product aldehydes can be recovered and converted to useful materials. For example, 2-ethylhexenal, which can result from the condensation of 2 molecules of n-butyraldehyde with each other, can be hydrogenated to form 2-ethylhexanal which can be used as first aldehyde in the aldol reaction (Procedure A).

The unsaturated aldehyde of formula (2) can be converted to a corresponding saturated aldehyde of the formula



in which; (a) x is 0 or an integer from 1 to 4; (b) y is 0 or an integer from 1 to 4; and (c) R is an alkyl group having 1 to 4 carbon atoms; by conventional hydrogenation techniques with hydrogen gas using Raney nickel as catalyst, a hydrogen pressure of 200—400 psig and a temperature of 100—200°C.

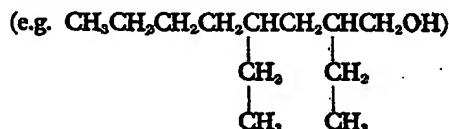
The unsaturated aldehyde of formula (2) or the saturated aldehyde of formula (3) can be converted to a corresponding alcohol having the formula



in which: (a) x is 0 or an integer from 1 to 4; (b) y is 0 or an integer from 1 to 4; and (c) R is an alkyl group having 1 to 4 carbon atoms, by conventional hydrogenation techniques with hydrogen gas using nickel, Raney nickel, platinum, or palladium as catalyst. Hydrogen pressures of for example, 400—500 psig at 100—200°C are operable.

The corresponding esters can be readily prepared by conventional esterification techniques. A preferred technique for preparing such an ester comprises:

Admixing about 2.2 moles of the alcohol of formula (4)



per mole of the dioic acid (e.g. azelaic acid), and a suitable catalyst (e.g. p-toluene sulphonic acid) to form a reaction mixture in a reaction zone provided with a heat source, agitating means, an inlet port, an outlet port, and a vent for removing by-product water as water vapour along with vaporized alcohol. It is generally preferred to use 2—2.2 moles of the alcohol per mole of the dioic acid. Unreacted alcohol can be recovered and reused. It is also generally preferred to use 0.2—0.4% (preferably 0.25%) of the catalyst based on the weight of the dioic acid plus the weight of the alcohol. The thus formed mixture is heated to its reflux temperature and maintained at a temperature effective for removing by-product water until substantially all of the dioic acid has been converted to the ester. Water and excess alcohol which boil off are condensed, and recovered as the reaction progresses. Water, being only slightly soluble in the alcohol can be separated from the recovered alcohol-water mixture. This produces a substantially water-free alcohol which can be recycled to the reaction zone.

Alternatively, toluene can be added to help remove by-product water. If such procedure is used toluene and water boil off. The toluene-water mixture can be condensed and recovered. The toluene can be separated from the water and recycled to the reaction zone. Some alcohol generally vaporizes along with the water and toluene. In such instance a mixture of alcohol and toluene can be separated and recycled. When the esterification has progressed to a predetermined degree, the excess alcohol and any unreacted dioic acid can be separated, and the product ester recovered.

#### EXAMPLE I

##### Run No. 1, With PTC

A 1 liter flask provided with an agitator means, a reflux condenser, a thermometer, a heating means, and an inlet port was charged with a solution of 33 g water, 14 g sodium hydroxide, and 9.4 g of a PTC (a commercially available tricaprylmethylammonium chloride).

A "dropping funnel" (addition funnel) was fitted into the inlet port of the 1 liter flask and an admixture of 72 g (1 mole) of n-butyraldehyde and 256 g (2 mole) of 2-ethylhexanal was added, via the dropping funnel, to the mixture in the one litre flask over a period of about 2 1/4 hours while agitating the resulting reaction mixture in said flask and while keeping the temperature of said reacting mixture at about 60°C.

The mixture in the flask was maintained at about 60°C for an hour after all of the admixture of n-butyraldehyde and 2-ethylhexanal had been added. It was then cooled to room temperature.

The cooled mixture was transferred from the 1 liter flask to a separating funnel and separated into an aqueous phase and an organic phase. The organic phase was washed with water until the wash water was neutral to litmus paper. The washed organic phase was dried (with anhydrous calcium sulfate), weighed (309 g), and placed in a container which was labeled "Example I, Product No. 1". The container was closed and set aside for analysis.

#### Run No. 2, Without PTC

The general procedure of Run No. 1 of this example (Example I) was repeated. However, in this instance the PTC was omitted. The dried organic phase obtained in this run weighed 297 g. It was placed in a container which was labeled "Example I, Product No. 2". The container was then closed to await analysis.

#### Run No. 3—Analysis of Products Nos. 1 and 2

The above described Products Nos. 1 and 2 prepared in this example were analyzed for product aldehyde(2,4-diethyloctenal, and unreacted reactant aldehydes (n-butyraldehyde and 2-ethylhexanal)) by fractional distillation and gas chromatography of the resulting fractions.

In the case of Product No. 1 (which was prepared with the PTC) it was found that 36% of the 2-ethylhexanal charged had reacted and that 89% of the 2-ethylhexanal which reacted was converted to the desired product aldehyde (2,4-diethyloctenal).

In the case of Product No. 2 (which was prepared without the PTC) it was found that only 20% of the 2-ethylhexanal charged had reacted and that only 45% of the 2-ethylhexanal which reacted was converted to the desired product aldehyde (2,4-diethyloctenal).

### EXAMPLE II

#### Run No. 1, With PTC

This run was made using the apparatus and general procedure used in Run No. 1 of Example I, supra. However, in this instance, reaction temperature was 95°C and the quantities charged were:

Material Charged	Quantity Charged, Moles
Water	7
NaOH	0.2
PTC*	0.02
2-ethylhexanal	2
n-butyraldehyde	1

\* Commercially available tricaprylmethylammonium chloride.

The admixture of 2-ethylhexanal and n-butyraldehyde was added over a period of 2 hours and the resulting reacting mixture was maintained at 95°C for about an hour after adding the admixture of these aldehydes.

The cooled dried organic phase product was placed in a container labeled "Example 2, Product No. 1", and the container was closed to await analysis of its contents.

#### Run No. 2, Without PTC

The general procedure of Run No. 1 of this Example (Example 2) was repeated. However, in this instance the PTC was omitted.

The cooled dried organic phase product was placed in a container labeled "Example 2, Product No. 2", and the container was closed and set aside for analysis.

#### Run No. 3—Analysis of Products Nos. 1 and 2

Products Nos. 1 and 2 (from Run Nos. 1 and 2, respectively, of this Example (Example 2)) were analyzed according to the general procedure used in Run No. 3 of Example I. It was found that Product No. 1 (from the run using the PTC) contained about 3 times as much of the desired 2,4-diethyloctenal as did Product No. 2 from the run without the PTC).

### EXAMPLE III

The general procedure of Run No. 1 of Example I was repeated. However, larger apparatus was used to accommodate larger quantities of materials used in this run. Said quantities were:

	Material Charged	Quantity Charged	
		g	Moles
5	Water	880	49
	Sodium Hydroxide	98	2.4
	PTC*	66	0.14
	n-butyraldehyde	504	7
	2-ethylhexanal	1792	14

\* The PTC was Aliquat 336 (commercially available tricaprylmethylammonium chloride).

10 The dried organic phase product obtained in this run was designated "Example III, Crude Product"; it was analyzed according to the general procedure used in Run No. 3 of Example I. 10

15 It was found that 384 g (2.98 moles) of the 2-ethylhexanal had reacted and that 350 g (1.92 moles) of the 2-ethylhexanal had been converted to 2,4-diethyl octenal. In other words, 65.8% of the 2-ethylhexanal which reacted was converted to the desired product (2,4-diethyloctenal). 15

#### EXAMPLE IV

20 This Example illustrates a preferred method for preparing our product aldehyde via a batch process in which a lower molecular weight reactant aldehyde (which corresponds to the second aldehyde of the above Summary) is added over a period of time to an admixture comprising water, alkali metal hydroxide, PTC, and a higher molecular weight reactant aldehyde (which corresponds to the first aldehyde of the above Summary). 20

25 256 g (2 moles) of 2-ethylhexanal, 14 g (0.35 mole of NaOH, 126 g (7 moles) of water, and 9.4 g (0.02 mole of a phase transfer catalyst (commercially available tricaprylmethylammonium chloride) were admixed in a 1 liter flask provided with an agitator means, a reflux condenser, a heating means, and an inlet port having an addition funnel positioned therein. The temperature of the resulting admixture was adjusted to 95°C and 72 g (1 mole) of n-butyraldehyde was added thereto (via the addition funnel) over a period of 5 hours while maintaining the temperature of the material in the flask at about 95°C to form a product mixture. 30

35 The product mixture was worked up and analyzed according to the general procedure set forth in Example I, supra. It was found that 25% of the 2-ethylhexanal had reacted, and that 95% of the reacted 2-ethylhexanal had been converted to the desired product, 2,4-diethyloctenal. 35

40 Where using the method illustrated by this example we generally add the lower molecular weight reactant aldehyde over a period of 1—6 hours while maintaining the mixture to which said lower molecular weight aldehyde is added at 60—110°C (preferably about 95°C). If desired the reacting mixture can be maintained about 60—110°C (preferably about 95°C) for a period of time (e.g. 1/2 to 2 hours) after all of the lower molecular reactant aldehyde has been added. Where using this method it is preferred to use about 1 mole of the lower molecular weight reactant aldehyde per 2 moles of the higher molecular weight reactant aldehyde. 40

#### EXAMPLE V

45 Preparation of 2,4-diethyloctanol 45

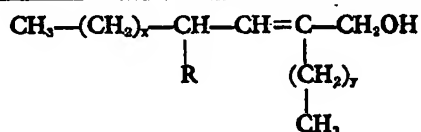
50 A 155.4 g portion of an aldehyde fraction boiling at 79—83°C at a pressure of 1 mm of mercury absolute which was obtained by distilling the above described "Example III, Crude Product" was analyzed by gas chromatography and found to contain 94.4% of 2,4-diethyloctenal (i.e. it obtained 146.6 g of 2,4-diethyloctenal). All this distilled material was admixed with about 1000 ml of hexane and hydrogenated at 140°C, under a hydrogen pressure of 440 psig using 1.5 g of Raney nickel as catalyst. 50

55 After about 4 hours the hydrogenation was completed. The hexane was then removed from the hydrogenated product by distillation. Analysis of the hydrogenated product showed that it contained 125.1 g of 2,4-diethyloctanol which means that 84% of the 2,4-diethyloctenal was converted to 2,4-diethyloctanol. 55

60 Similar results can be obtained by this procedure in the absence of the hexane which was added as a solvent and diluent because of the small amount of the aldehyde being hydrogenated in a large apparatus. 60

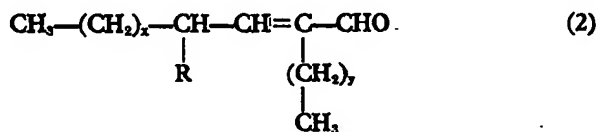
An alcohol having the formula





in which x is an integer from 0 to 4, y is an integer from 0 to 4, and R is an alkyl group having 1—4 carbon atoms can be formed by hydrogenating an aldehyde having the formula

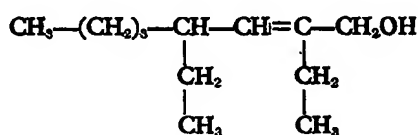
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(in which x, y, and R are as defined above) under mild conditions (e.g. at a temperature of 10—50°C, (usually 15—25°C), and under a hydrogen pressure of 0.5—2 atmospheres, (usually about 1 atmosphere). Where x is 3, y is 1, and R is —CH<sub>2</sub>CH<sub>3</sub>, the resulting alcohol is

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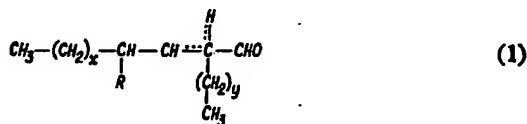
Such unsaturated alcohols are useful because they can be further hydrogenated to produce saturated alcohols useful for preparing esters which are useful as base stock for lubricants.

#### WHAT WE CLAIM IS:—

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1. A process of preparing an aldehyde having the general formula:

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wherein

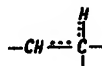
x is 0, 1, 2, 3 or 4,

y is 0, 1, 2, 3 or 4,

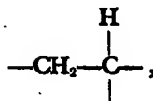
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R represents an alkyl group having 1 to 4 carbon atoms, and the symbol

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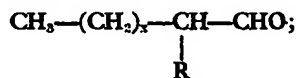
represents either the unsaturated group —CH=C— or the saturated group,



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which process comprises reacting  
(i) a first aldehyde having the formula

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with

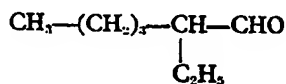
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(ii) a second aldehyde having the formula CH<sub>3</sub>—(CH<sub>2</sub>)<sub>y</sub>—CH<sub>2</sub>—CHO; in a reaction medium comprising an aqueous alkali metal hydroxide solution and a phase transfer catalyst, thereby producing an unsaturated aldehyde; and then if desired, hydrogenating the unsaturated aldehyde.

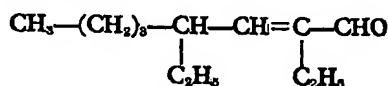
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2. A process according to claim 1, wherein there is used a first aldehyde in which R represents an ethyl group.

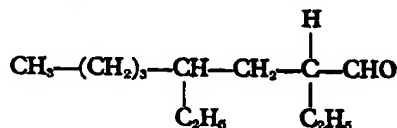
3. A process according to claim 2, wherein there is used a first aldehyde of formula



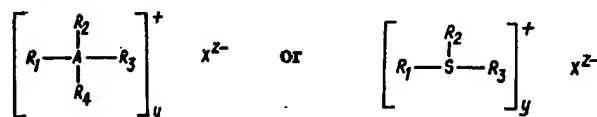
and a second aldehyde of formula  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$ , whereby there is formed the unsaturated aldehyde of formula



which, if desired, is then hydrogenated to the saturated aldehyde of formula



4. A process according to claim 1, wherein the phase transfer catalyst is a compound of formula



in which:

$X^{z-}$  represents an anion;

$z$  is an integer denoting the number of negative charges on each anion;

$y$  is an integer equal to  $z$ ;

and the R groups, viz  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  in the first formula and  $R_1$ ,  $R_2$  and  $R_3$  in the second formula, are separately selected from (i) alkyl and alkenyl groups having 1 to 20 carbon atoms, and (ii) aralkyl groups having 7 to 16 carbon atoms; and

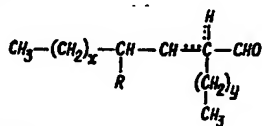
A represents N, P or As.

5. A process according to claim 4 wherein the phase transfer catalyst is any of those hereinbefore listed.

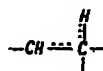
6. A process according to claim 1, substantially as hereinbefore described in "Procedure A".

7. A process according to claim 1 substantially as described in Example I, Run No. 1, Example II, Run No. 1, Example III, Example IV, or the combination of Examples III and V.

8. Aldehydes of formula

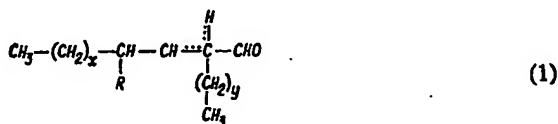


wherein  $x$ ,  $y$ , R and the symbol



are as defined in claim 1, when prepared by a process claimed in any preceding claim.

9 Aldehydes having the general formula



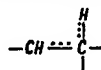
wherein

x is 1, 2, 3 or 4,

y is 0, 1, 2 or 3,

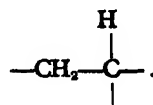
R is an alkyl group having 1 to 4 carbon atoms and the symbol

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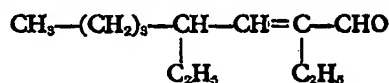


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represents either the unsaturated group  $-\text{CH}=\text{C}-$  or the saturated group



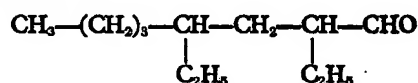
10. An aldehyde having the formula



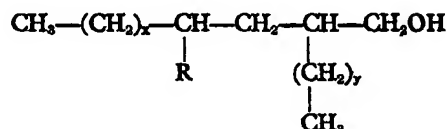
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11. An aldehyde having the formula

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12. A process of preparing an alcohol of formula



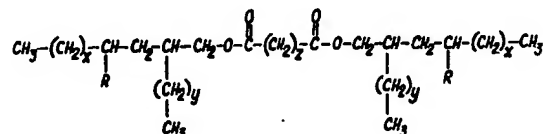
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where x, y and R are as defined in claim 1, which process comprises hydrogenating an unsaturated or saturated aldehyde claimed in claim 8, 9, 10 or 11.

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13. Alcohols when prepared by a process claimed in claim 12.

14. A process of preparing an ester having the formula



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x is 0, 1, 2, 3 or 4,  
in which

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y is 0, 1, 2, 3 or 4,

R represents an alkyl group having 1 to 4 carbon atoms, and

z is an integer from 1 to 12, provided that at least one of x and y is 0,

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which process comprises reacting an alcohol claimed in claim 13 with an alkane dicarboxylic acid of formula  $\text{HOOC}-(\text{CH}_2)_z-\text{COOH}$  where z is an integer from 1 to 12, using at least 2 moles of the alcohol per mole of the acid.

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15. Esters when prepared by a process claimed in claim 14.

J. A. KEMP & CO  
Chartered Patent Agents  
14 South Square  
Gray's Inn  
London WC1R 5EU.

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